Reagent Code Lists for Aiding Beginning Students in Determining the Structure of an Organic Chemistry Reaction Product.

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Abstract:

Use of reagent code lists allows beginning organic chemistry students to identify the net reactive species, i.e. the "code" for an organic reaction when a set of reagents, solvents and or catalysts are given. For example, the reagent pair dichromate/acid "codes" for oxygen, although not actually present, as the net reactive species. This code allows easier prediction of oxidation reactions with alcohols, alkenes and other groups. The reagent group mercury trifluoro acetate/water/sodium borohydride "codes" for addition of water to an alkene. When presented in tabular format, with reactant, reagent code, active species and product given, the students more easily follow the lecture. The instructor may present the reactions on the board or with slides, then refer the students to the appropriate "reaction codes" on the list. This process allows greater organization of the lecture for both instructor and student, and gives the student an understanding of what is actually occurring in an organic reaction when a series of reagents, solvents and or catalysts is presented for a reaction. Predicting the product becomes much easier and students indicate that they learn the reactions at a faster rate.

Discussion

Many beginning organic chemistry students initially have great difficulty with reactions, where, above or below the arrows, a series of reactants, solvents and /or catalysts are written. Without any previous exposure to many of these, they often do not understand how the set of reagents translates to, or "codes" to a reactive species such as oxygen, hydride ion, a carbanion etc. Once they understand the "code" for the reagent set with a reactant, they more easily predict reaction products. While teaching organic chemistry lecture over the last several years, I have generated "code lists" to help students recognize the actual and or net reactive species for the code. For example, sodium borohydride and lithium aluminum hydride "code" to a hydride ion, H^-, which, although not actually present, aids in predicting reactions with carbonyl compounds. A Grignard reagent codes to a "net" carbanion as reactive species. Even though this species does not actually form in the mechanistic sequence, thinking of a Grignard as an "R^- "allows easier prediction of reaction products with carbonyls or acids. Likewise, sodium nitrite/acid codes to nitrous acid, which with primary aromatic amines in turn codes to a "net" , if fictitious, phenyl carbocation. For the students, thinking of sodium nitrate/acid "coding" to phenyl carbocations, $C_6H_5^+$, with aromatic amines as starting material, allows easy predictions of products with halide, water, cyanide or other nucleophiles. Student feedback over five years indicates quicker assimilation of these reactions for exams, and allow for easier organization of the assigned material. The tables also list any limitations and stereochemistry for the reactions if appropriate.

Tables 1-XIV give code lists for the most common sophomore organic chemistry reactions, in roughly the order presented in the introductory organic texts. Lists are presented through carbohydrate chemistry. Instructors may modify these tables or change the sequence if they desire. The texts in the references,[1,2] were employed in generating these lists.

The author welcomes any comments or feedback on the utility of this organic chemistry teaching aid.

Table 1

Reagent code list for preparation

and reactions of alkenes

	REACTIONS OF	ALKENES	CODE	LIST
STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	STEREOCHEMISTRY
ALKENE	HCl HBr or HI/H_2O	HCL, HBr or HI	ALKYL HALIDE	MARKONIKOV
ALKENE	$Hg(OAC)_2/NaBH_4$ or H2O/H+	HOH	ALCOHOL	MARKONIKOV
ALKENE	Br_2/CCl_4 or Cl_2/CCL_4	Br_2, Cl_2	DIHALIDE	TRANS
ALKENE	Br_2/H_2O or Cl_2/H_2O	HOBr, HOCl	HALOHYDRIN	MARKONIKOV*, TRANS *Cl^+, $Br^+ = H^+$
ALKENE	RCOOOH (peracid)	O	EPOXIDE	RETENTION OF ALKENE STEREOCHEMISTRY
ALKENE	$Hg(OAC_2),H_2O$,THF $NaBH_4$	HOH	ALCOHOL	MARKONIKOV
1,2-DIOL	HIO_4	O	ALDEHYDES	
ALKENE	BH_3/THF OH^-, H_2O_2, H_2O	HOH	ALCOHOL	ANTI-MARKONIKOV, CIS
ALKENE	H_2/Pt or Pd, or D_2/Pt or Pd	H_2, D_2	ALKANE	CIS
ALKENE	OSO_4	2 OH ADD	DIOL	CIS
ALKENE	O_3/Zn	O	ALDEHYDE OR KETONE SEE CHART	
ALKENE	$KMNO_4$/H3O+	O	ACID OR CO_2 SEE CHART	
ALKENE	$CHCl_3/OH^-$	CCL_2, CARBENE	DICHLORO CYCLOPROPANE	RETENTION OF ALKENE STEREOCHEMISTRY
ALKENE	CH_2I_2/Zn	CH_2, CARBENE	CYCLOPROPANE	RETENTION OF ALKENE STEREOCHEMISTRY

Table 11

Reagent code list for preparation

and reactions of alkynes

STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	STEREOCHEMISTRY
TERMINAL ALKYNE R-C≡CH	HCl HBr or HI/H_2O, 1 MOLE	HCl, HBr or HI	VINYL HALIDE R-C=CH_2 | Cl	MARKONIKOV
TERMINAL ALKYNE R-C≡CH	HCl HBr or HI/H_2O, 2 MOLES	HCl, HBr or HI	2,2-DIHALOALKANE R-C-CH_3 | Cl	MARKONIKOV
TERMINAL ALKYNE R-C≡CH	Hg^{+2}/H_2SO_4 or H_2O/H+	HOH	METHYL KETONE $RCOCH_3$ VIA ENOL R-C=CH_2 | OH	MARKONIKOV
TERMINAL ALKYNE R-C≡CH	Br_2/CCl_4 or Cl_2/CCl_4 1 MOLE	Br_2, Cl_2, 1 MOLE	TRANS-DIHALOALKENE R-C=CH | | Br Cl	TRANS
TERMINAL ALKYNE R-C≡CH	Br_2/CCl_4 or Cl_2/CCl_4, 2 MOLES	Br_2, Cl_2, 2 MOLES	TETRAHALOALKANE R-C-CH | | Br Br	NOT APPLICABLE
TERMINAL ALKYNE R-C≡CH	BH_3 OR ISOAMYLBORANE/THF OH^-, H_2O_2, H_2O	HOH	ALDEHYDE RCH_2CHO VIA ENOL RCH=CHOH	ANTI-MARKONIKOV
TERMINAL ALKYNE R-C≡CH	H_2/Pt OR Pd (2MOLES)	H_2, 2 MOLES	ALKANE RCH_2CH_3	NOT APPLICABLE
TERMINAL ALKYNE R-C≡CH	1) $NaNH_2$, 2) R'-X R= PRIMARY HALIDE X= Br or Cl	R'-X	INTERNAL ALKYNE R-C≡CR'	NOT APPLICABLE
INTERNAL ALKYNE R-C≡CR'	HCl HBr or HI/H_2O, 1 MOLE	HCl, HBr or HI 1MOLE	VINYL HALIDE RC=CHR' | Cl	NOT APPLICABLE

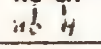
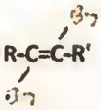
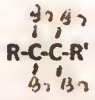
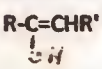
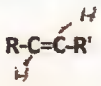
STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	STEREOCHEMISTRY
INTERNAL ALKYNE R-C≡CR'	HCl HBr or HI/H_2O, 2 MOLE	HCl, HBr or HI 2 MOLES	DIHALOALKANE 	NOT APPLICABLE
INTERNAL ALKYNE R-C≡CR'	Hg^{+2}/H_2SO_4 or H_2O/H+	HOH	KETONE $RCOCH_2R'$ VIA ENOL $RC{=}CR'$ 	NOT APPLICABLE
INTERNAL ALKYNE R-C≡CR'	Br_2/CCl_4 or Cl_2/CCl_4 1 MOLE	Br_2, Cl_2, 1 MOLE	TRANS-DIHALOALKENE 	TRANS
INTERNAL ALKYNE R-C≡CR'	Br_2/CCl_4 or Cl_2/CCl_4, 2 MOLES	Br_2, Cl_2, 2 MOLES	TETRAHALOALKANE 	NOT APPLICABLE
INTERNAL ALKYNE R-C≡CR'	BH_3 OR ISOAMYLBORANE/THF OH^-, H_2O_2, H_2O	HOH	KETONE $RCOCH_2R'$ VIA ENOL 	NOT APPLICABLE
INTERNAL ALKYNE R-C≡CR'	H_2/Pd/$BaSO_4$ LINDLAR CATALYST	H_2, 1 MOLE	CIS-ALKENE 	CIS
INTERNAL ALKYNE R-C≡CR'	Na OR Li/NH_3	H_2, 1 MOLE	TRANS-ALKENE 	TRANS
INTERNAL ALKYNE R-C≡CR'	H_2/Pt OR Pd (2MOLES)	H_2, 2 MOLES	ALKANE RCH_2CH_2R'	NOT APPLICABLE

Table 111

Reagent code list for preparation

of alkyl halides

ORGANOHALIDES CODE LIST

STARTING MATERIAL	REAGENT CODE	MECHANISM	PRODUCT	USES
Alkene	HCl HBr, HI	Carbocation	Markonikov	Preparation of Alkyl Halide
Alkene	Cl_2/light, Br_2/light	Free Radical	R-Cl, R-Br	Preparation of Alkyl Halide Cl_2 not selective Br_2 selective
Alkene	NBS	Free Radical	R-Br	Allylic Bromination Unless Alkene Symmetrical Product Mixture
Alkene	Cl_2/CCl_4, Br_2/CCl_4	Cyclic Br^+ Cl^+	Trans dihalide	Preparation of Dihalide
ROH	Hl, or HCL, or HBr	SN1 or SN2	RCl, RBr, RI	Reagents for SN1, SN2 displacements No Prim or sec alcohol
ROH	PBr_3	Cyclic	RBr	Reagents for SN2 displacements No Tertiary alcohol
ROH	$SOCl_2$	Cyclic	RCl	Reagents for SN2 displacements No Tertiary alcohol
ROH	Tosyl Chloride	DONT NEED	ROTS	Excellent leaving group for SN2 displacements No Tertiary alcohol
RX X = Halogen	Mg /ether or THF	DONT NEED	R-MgX	Preparation of Grignard Reagent Source of Strong base R^-
RX X = Halogen	Li /ether or THF	DONT NEED	R-Li	Preparation of Organolithium Compound Source of Strong base R^-
RLi	CuI	DONT NEED	$(R)_2CuLi$	Preparation of Gilman Reagent
RX X = Halogen	$(R')_2CuLi$	DONT NEED	R-R'	Coupling of alkyl or aryl groups, Gilman Reagent Source of Strong base R^-
R-Mg-X X= Halogen	HOH or DOD	DONT NEED	R-H OR R-D	Alkane synthesis, isotopically labled alkanes

Table IV

Reagent code list for reactions

of alkyl halides

REACTIONS OF ALKYL HALIDES CODE LIST

STARTING MATERIAL	REAGENT CODE	MECHANISM	PRODUCT	STEREOCHEMISTRY
1^{o} OR 2^{o} alkyl halide	Nucleophile	SN2	Substitution	Inversion
3^{o} alkyl halide	Nucleophile	SN1	Substitution	Racemization
1^{o} OR 2^{o} alkyl halide	Nucleophile with heat	E2	Alkene	Trans-Coplanar for H and Halide Usually gives most substituted alkene unless trans coplanar arrangement cannot result in most substituted alkene
3^{o} alkyl halide	Nucleophile with heat	E1	Alkene	Carbocation intermediate Always gives most substituted alkene

Table V

Reagent code list for reactions

of aromatic compounds

REACTIONS OF AROMATICS

CODE: EAS = Electrophilic Aromatic Substitution; NAS = Nucleophilic Aromatic Substitution

LIST: Ar = C_6H_5

STARTING MATERIAL	REAGENT CODE	ACTIVE SPECIES	MECHANISM	PRODUCT	USES	LIMITATIONS
Ar-H	$Br_2/FeBr_3$	Br^+	EAS	Ar-Br	Halogenation	None
Ar-H	$Cl_2/FeBr_3$	Cl^+	EAS	Ar-Cl	Halogenation	None
Ar-H	I_2/HNO_3	I^+	EAS	Ar-I	Halogenation	None
Ar-H	HNO_3/H_2SO_4	NO_2^+	EAS	$ArNO_2$	Nitration	None
Ar-H	H_2SO_4	HSO_3^+	EAS	$ArSO_3H$	Sulfonation	None
Ar-H	RCl or RBr/ $AlCl_3$	R^+ R cannot be Ar or $H_2C{=}CH$-	EAS	Ar-R	Alkylation	Carbocation Rearranges
Ar-H	RCOCl	RCO^+	EAS	ArCOR	Acylation	None
ArCOR	Zn/HCl H_2/Pt	H_2	Reduction	$ArCH_2R$	Aryl ketone reduction	None
$ArCH_3$	NBS	$Br^{\cdot}$	Free radical halogenation	$ArCH_2Br$	Allylic halogenation	None
$ArNO_2$	Fe/HCl or Zn/HCl or H_2/Pd	H_2	Reduction	$ArNH_2$	Nitro reduction	None
$ArCH_3$ OR	$Na_2Cr_2O_7/H^+$ $KMnO_4/H+$	O	Oxidation	ArCOOH	Side Chain Oxidation	None
$ARCH_2R$	$Na_2Cr_2O_7/H^+$ $KMnO_4/H+$	O	Oxidation	ArCOOH	Side Chain Oxidation	None
$ArCH{=}CH_2$	H_2/Pt	H_2	Reduction	$ArCH_2CH_3$	Regular double bond reduced aromatics no	None
$Ar(NO_2)_3Cl$	$Nu:^-$ Nu:- = OH^- or other nucleophile	$Nu:^-$	Substitution NAS	$Ar(NO_2)_3Nu$	Need Nitro or other electron withdrawing groups	

Table V1

Reagent code list for preparation and reactions

of alcohols

REACTIONS OF ALCOHOLS CODE LIST

STARTING MATERIAL	REAGENT CODE	Reactive Species	PRODUCT	STRUCTURE
ROH	NaH or $NaNH_2$	H^- or NH_2-	Alkoxide Salt	$RO^- Na^+$
1° Alcohol RCH_2OH	Dichromate or Permanganate/acid	O	Acid	RCOOH
2° Alcohol RCHOHR'	Dichromate or Permanganate/acid	O	Ketone	RCOR'
Alkene	Borane/peroxide	HOH	Alcohol	Anti-Markonikov, cis
Alkene	Hg salt/water	HOH	Alcohol	Markonikov
Alkene	OSO_4	O	diol	cis diol
$H_2C=O$	$NaBH_4$	H-	Primary alcohol	CH_3OH
$H_2C=O$	$LiAlH_4$	H-	Primary alcohol	CH_3OH
RCH=O(aldehyde)	$NaBH_4$	H-	Primary alcohol	RCH_2OH
RCH=O(aldehyde)	$LiAlH_4$	H-	Primary alcohol	RCH_2OH
RCH=O(aldehyde)	R'MgBr	R-	Sec Alcohol	RR'CHOH
RC=OR' (ketone)	R''MgBr	R-	Tert Alcohol	RR'R''OH
RC=OR' (ketone)	$NaBH_4$	H-	Sec Alcohol	RR'CHOH
RC=OR' (ketone)	$LiAlH_4$	H-	Sec Alcohol	RR'CHOH
RC=OOR (ester)	$NaBH_4$	H-	NR	
RC=OOR (ester)	R'MgBr (2 moles)	R-	Tert Alcohol	RR'R'OH
RC=OOR (ester)	$LiAlH_4$	H-	Primary alcohol	RCH_2OH
RCOOH, acid	$NaBH_4$	H-	NR	
RCOOH, acid	$LiAlH_4$	H-	Primary alcohol	RCH_2OH
3° Alcohol	HX X = halide	Carbocation	Halide	RX

2° or 1°Alcohol	PBr_3 or $SOCl_2$	SN2	Halide	RBr or RCl
ROH	TsCl	ROTs	Tosylate	good leaving group
ROH	Acid or $POCl_3$	Carbocation	Alkene	Zaitsev Product
ROH	R'COOH/acid	ROH	Ester	RCOOR'
1°Alcohol RCH_2OH	PCC	O	Aldehyde	RCH=O
2°Alcohol RCHOHR'	PCC	O	Ketone	RCOR'

Table VII

Reagent code list for preparation and reactions

of ethers, epoxides, thiols and sulfides

REACTIONS OF ETHERS THIOLS OR SULFIDES CODE LIST

STARTING MATERIAL	REAGENT CODE	Reactive Species	PRODUCT	STRUCTURE	Limitation
RBr	NaOR	RO-	ETHER	ROR'	R not 3^{o}
ROH	CH_3I/Ag_2O	CH_3I	Methyl Ether	$ROCH_3$	None
Alkene	1) Hg salt, R'OH 2) $NaBH_4$	R'OH	ETHER	ROR'	Markonikov Addition R'OH
Ether, ROR'	HX, H=Halogen	HX	Alcohol + Halide	ROH +R'X	If R and R' = 1^{o} or 2^{o} X attacks less hindered if 3^{o} X attacks 3^{o}
Allyl Phenyl Ether	Heat, Rearranges	Concerted	o-allyl phenol	o-allyl phenol	None
Alkene	Peracid RCOOOH	O	Epoxide	Cis addition	None
Halohydrin	Base	Alkoxide	Epoxide	Cis epoxide	None
Epoxide	H_2O	H_2O	1,2 diol	Trans	None
Epoxide	HX, H=Halogen	HX	Halohydrin		If R and R' = 1^{o} or 2^{o} X attacks less hindered if 3^{o} ,X attacks 3^{o}
Epoxide	Base	HO^-	Diol	Trans	HO^- attacks less hindered side
Ethylene Oxide	RMgBr	R^-	Alcohol	RCH_2CH_2OH	None

STARTING MATERIAL	REAGENT CODE	Reactive Species	PRODUCT	STRUCTURE	Limitation
RX X= halogen	NaSH	HS-	Thiol	RSH	low yield
RX X= halogen	Thiourea	Thiourea	Thiol	RSH	none
RSH	I_2 or peroxide	O	disulfide	RSSR	none
RX X= halogen	NaSR'	RS-	sulfide	RSR'	R no 3° SN2
RSR'	Peroxide	O	Sulfoxide	RS=OR'	none
RS=OR'	Peracid	O	Sulfone	RSO2R'	none

Table VIII

Reagent code list for preparation and reactions

of aldehydes and ketones

ALDEHYDES	AND	KETONES	CODE	LIST
STARTING MATERIAL	CODE	REACTIVE SPECIES	PRODUCT	MECHANISM
1° Alcohol	PCC	O	aldehyde	N/A
Ester	DIBAH	H^-	Aldehyde	H^- Attack on C=O
Acid Chloride	R_2CuLi	R^-	Ketone	R^- Attack on C=O
Aldehyde	CrO_3 or other strong O agent	O	Acid	N/A
Aldehyde or Ketone	$NaBH_4$ or LAH	H-	Alcohol	H^- Attack on C=O
Aldehyde or Ketone	RMgBr	R^-	Alcohol	R^- Attack on C=O
Aldehyde or Ketone	HCN	CN^-	Cyanohydrin	CN^- Attack on C=O
Aldehyde or Ketone	RNH_2	NH_2	Imine	RNH_2 Attack on C=O
Aldehyde or Ketone	2° Amine R_2NH	R2NH	Enamine	R_2NH Attack on C=O
Aldehyde or Ketone	H_2NNH_2/Base	H_2NNH_2	Hydrocarbon	H_2NNH_2 attack on C=O
Aldehyde or Ketone	ROH 1 mole	ROH	Hemiacetal	ROH Attack on C=O
Aldehyde or Ketone	ROH 2 moles	ROH	Acetal	ROH Attack on Hemiacetal
Aldehyde or Ketone	Wittig Reagent	Wittig Reagent	Alkene	Wittig attack on C=O
Alpha-Beta Unsaturated Aldehyde or Ketone	Nu^-	Nu^-	Beta adduct	Nu- attack on C=C

ALKENE	O_3	O	Aldehyde or Ketone	O Cleaves C=C
Aromatic	Acyl Chloride/ Aluminum chloride	RCO+	Aryl Ketone	RCO + Attacks Ring
Terminal Alkyne	Hg Salt/HOH/ NaBH4	HOH	Methyl Ketone	HOH adds Markonikov
Aldehyde or Ketone	HOH	HOH	1,1 diol	HOH attacks C=O

Table IX

Reagent code list for preparation and reactions

of carboxylic acids

PREPARATION AND REACTIONS OF CARBOXYLIC ACIDS				CODE LIST
STARTING MATERIAL	REAGENT CODE	Active Species	PRODUCT	LIMITATION
Acids RCOOH	OH^-	OH^-	Salts, RCOONa	
Salts, RCOONa	R'X	$RCOO^-$	Esters RCOOR'	SN_2 No 3°
Acids RCOOH	R'OH	R'OH	Esters RCOOR'	
Acids RCOOH	LAH	H^-	1° Alcohols RCH_2OH	
Acids RCOOH	$SOCl_2$	$SOCl_2$	Acid Chlorides RCOCl	
Acid Chlorides RCOCl	R'OH	R'OH	Esters RCOOR'	
Acid Chlorides RCOCl	NH_3	NH_3	Amides, $RCONH_2$	
Alkyl Benzenes	$KMNO_4/H^+$ Or CrO_3	O	Benzoic acids ArCOOH	
Alkenes	$KMNO_4/H^+$ Or CrO_3	O	Carboxylic acids RCOOH	
1° Alcohols	$KMNO_4/H^+$ Or CrO_3	O	Carboxylic acids RCOOH	
Aldehydes	$KMNO_4/H^+$ Or CrO_3	O	Carboxylic acids RCOOH	
RX X = Hal or OTS	CN^-	CN^-	Nitriles RCN	SN_2 No 3°
Nitriles RCN	H_3O^+ Full Hydrolysis	H_3O^+	Carboxylic acids RCOOH	
Nitriles RCN	H_3O^+ Partial Hydrolysis	H_3O^+	Amides $RCONH_2$	
Grignards RMgBr	1) CO_2	R^-	Carboxylic acids	

Amides, $RCONH_2$	$POCl_3$ Dehydrate	$POCl_3$	Nitriles RCN
Amides, $RCONH_2$	H_3O^+ Hydrolysis	H_3O^+	Carboxylic acids RCOOH
Nitrile RCN	LAH	H^-	1^o Amines RCH_2NH_2
Amides, $RCONH_2$	LAH	H^-	1^o Amines RCH_2NH_2
Nitriles RCN	1) Grignard R'MgBr 2) H_3O^+ Hydrolysis	R^-	Ketones RCOR'

Table X

Reagent code list for preparation and reactions of carboxylic acid chlorides, esters, anhydrides and amides

PREPARATION AND REACTIONS OF CARBOXYLIC ACID DERIVATIVES CODE LIST

NU = NUCLEOPHILE

STARTING MATERIAL	REAGENT CODE	NU	PRODUCT
ACID RCOOH	SOCl2	NA	ROCl
RCOOH	P2O5 dehydrate	NA	RCOOCOR anhydride
RCOO- Na+ ACID SALT	R'X R = 1°	RCOO-	RCOOR' ESTER
RCOOH	R'OH	R'OH	RCOOR' ESTER
RCOCl ACID CHLORIDE	R'OH	R'OH	RCOOR' ESTER
RCOCl	R'COO- Na+	RCOO-	RCOOCOR' anhydride
RCOCl	H2O	H2O	RCOOH ACID
RCOCl	R'NH2	NH2	RCONHR' 2° AMIDE
RCOCl	RR''NH	NH	RCONR'R'' 3° AMIDE
RCOCl	NH3	NH3	RCONH2 AMIDE
RCOCl	DIBAH	H-	RCOH ALDEHYDE
RCOCl	LAH	H-	RCH2OH 1° ALCOHOL
RCOCl	RMgBr	R-	RR'R'COH 3° ALCOHOL

RCOOR' ESTER	H2O	H2O	RCOOH ACID
RCOOR'	OH-	OH-	R'COO- Na+ ACID SALT
RCOOR'	NH3	NH3	RCONH2 AMIDE
RCOOR'	R'NH2	NH2	RCONHR' 2° AMIDE
RCOOR'	RR''NH	NH	RCONR'R'' 3° AMIDE
RCOOR'	DIBAH	H-	RCOH ALDEHYDE
RCOOR'	LAH	H-	RCH2OH 1° ALCOHOL
RCOOR'	R''MgBr 2 MOLES	R-	RR''R''COH 3° ALCOHOL
RCONH2 AMIDE	POCL3 DEHYDRATE	NA	RCN NITRILE
RCONH2	LAH	H-	RCH2NH2 1° AMINE
RCONH2	H3O+ HEAT	H2O	RCOOH ACID
RCONH2	OH-	OH-	R'COO- Na+ ACID SALT
RCONHR' 2° AMIDE	LAH	H-	RCH2NHR' 2° AMINE
RCONR'R'' 3° AMIDE	LAH	H-	RCH2NRR'' 3° AMINE
RCN NITRILE	LAH	H-	RCH2NH2 1° AMINE
RCN	H3O+	H2O	RCOOH

			R'COO- Na+
RCN	OH-	OH-	ACID SALT
	1) R'MgBr	R-	RCOR'
RCN	2) H3O+		KETONE

Table XI

Reagent code list for carbonyl

alpha-substitution reactions

CARBONYL ALPHA SUBSTITUTION REACTIONS CODE LIST

STARTING MATERIAL	REAGENT CODE	NU⁻	PRODUCT	STRUCTURE
Aldehyde or ketone with alpha hydrogens $RCH_2C{=}O(H)(R)$	X_2/H^+ X= Cl_2 or Br_2 or I_2	Enol	alpha halo aldehyde or ketone	$XCH_2C{=}O(H)(R)$ X = halogen
Aldehyde or ketone with alpha hydrogens $RCH_2C{=}O(H)(R)$	X_2/OH^- X= Cl_2 or Br_2 or I_2	Enolate $RCH^-C{=}O(H)(R)$	alpha di-halo aldehyde or ketone brominates two times	$X_2CC{=}O(H)(R)$ X = halogen
Methyl ketone $R\text{-}COCH_3$	X_2/OH^- X= Cl_2 or Br_2 or I_2	Enolate $R\text{-}COCH_2^-$	Acid brominates three times	RCOOH Haloform Reaction
Acid with alpha Hydrogens RCH_2COOH	1)PBr_3/Br_2 2) H^+	Enol	alpha-halo acid	Hell Volhard Zelinsky reaction RCHBrCOOH
alpha halo aldehyde or ketone $RCH_2CHXCOR'$ X=Hal	Amine/heat Dehydro halogenate	NA	alpha-beta unsaturated aldehyde/ketone	RCH=CHCOR'
Aldehyde or ketone or ester or nitrile with alpha hydrogens $RCH_2C{=}O(H)(R)$	1) LDA 2) R'X X= halogen SN2	Enolate $RCH^-C{=}O(H)(R)$	alpha-alkylated product	$RR'CHC{=}O(H)(R)$
Malonic ester $CH_3CH_2OCOCH_2COOCH_2CH_3$	1) Base, OR^- 2) R'X, SN2 3) H+ lose CO_2	Enolate	Acid	$R'CH_2COOH$
Acetoacetic ester $CH_3COCH_2COOCH_2CH_3$	1) Base, OR^- 2) R'X, SN2 3) H+ lose CO_2	Enolate	Methyl Ketone	CH_3COCH_2R'

Table XII

Reagent code list for carbonyl

condensation reactions

CARBONYL CONDENSATION REACTIONS			CODE	LIST
STARTING MATERIAL	REAGENT CODE	NU^-	PRODUCT	STRUCTURE
Aldehyde or ketone with alpha hydrogens $R\text{-}COCH_3$	1) Base, OR^- self condensation two moles	Enolate $R\text{-}COCH2^-$	beta-hydroxy ketone $RCOCH_2CCH_3$ may lose H_2O to give alkene $RCOC{=}CCH_3$	Aldol Condensation
MIXED ALDOL POSSIBLE IF	ONE ALDEHYDE OR	KETONE HAS	NO ALPHA	HYDROGENS
IF BOTH IN	SAME MOLECULE A	CYCLIC	beta-hydroxy ketone	RESULTS
Ester with Alpha Hydrogens CH_3COOCH_3	1) Base, OR^- self condensation two moles	Enolate $CH_2^-COOCH_3$	beta-keto ester	Claisen Condensation $CH_3COCH_2COOCH_3$
MIXED CLAISEN POSSIBLE IF	ONE ESTER	HAS	NO ALPHA	HYDROGENS
IF BOTH IN	SAME MOLECULE A	CYCLIC	BETA DIKETONE	RESULTS
$H_2C{=}CH\text{-}C{=}O(H)(R)$ alpha, beta unsat ketone	beta diketone $RCOCH_2COCH_3$ /OR-	Enolate $RCOCH^-COCH_3$		Michael Reaction $NUCH_2CH_2C{=}O(H)R$ NU= $RCOCH^-COCH_3$ Congugate addition
$H_2C{=}CH\text{-}C{=}O(H)(R)$ alpha, beta unsat ketone	1) Enamine	Enolate		$RCOCH_2CH_2C{=}O(H)(R)$ Stork Modification of Michael Reaction Congugate addition

Table XIII

Reagent code list for preparation

and reactions of amines

PREPARATION AND REACTIONS OF AMINES CODE LIST

STARTING MATERIAL	REAGENT CODE	MECHANISM	PRODUCT	USES	LIMITATIONS
Nitrile RCN	LAH	H- Reduction	RCH_2NH_2	1° Amine Prep	None
Amide $RCONH_2$	LAH	H- Reduction	RCH_2NH_2	1° Amine Prep	None
Primary Alkyl Halide RCH_2Br	NH_3	SN2	Primary Amine RCH_2NH_2	Bulk preparation of amines	Gives mixtures with sec, tert amines
Primary Amine RCH_2NH_2	Primary Alkyl Halide RCH_2Br	SN2	Sec Amine $(RCH_2)_2NH$	Bulk preparation of amine	Gives mixtures with tert amines
Sec Amine $(RCH_2)_2NH$	Primary Alkyl Halide RCH_2Br	SN2	Tert Amine $(RCH_2)_3N$	Bulk preparation of amine	Gives mixtures with quat amines
Tert Amine $(RCH_2)_3N$	Primary Alkyl Halide RCH_2Br	SN2	"Quat" Amine $(RCH_2)_4N^+ Br^-$	Bulk preparation of Soaps	None
Phthalamide	Primary Alkyl Halide RCH_2Br	SN2	Primary Amine RCH_2NH_2	Prep primary amine no sec or tert byproduct	No sec or tert halide
Primary Alkyl Halide RCH_2Br	Sodium Azide NaN_3	SN2	Primary Alkyl Azide RCH_2N_3	Reactive Synthetic intermediate	Must be Primary Halide
Primary Alkyl Azide RCH_2N_3	H_2/Pd or LAH	Reduction	Primary Amine RCH_2NH_2	High yields of Primary amine	None
Aldehyde/ketone RCH2CHOH(R)	1,NH_3 2) LAH	Reduction	Prim or sec Amine	High yields of amine	None
Amide $RCONH_2$	1) OH^- Br_2	Isocyanate Intermediate	Primary Amine RNH_2	Amine with one less carbon	None Hoffman Degradation
Acid Chloride RCOCl	1)NaN_3 2) Heat -CO_2	Isocyanate Intermediate	Primary Amine RNH_2	Amine with one less carbon	None Curtius Rearrangement

$ArNH_2$ Aromatic Amine	HONO Nitrous acid		ArN_2^+ Diazonium salt	Source of Ar+	None
ArN_2^+ Diazonium salt	HX CuX X= hal	X^- on Ar^+	ArCl or ArBr or ArI	Prep Halobenzenes	None
ArN_2^+	CuCN	CN^- on Ar^+	ArCN	Prep Aromatic Nitriles	None
ArN_2^+	Cu_2O/H_2O	OH^- on Ar^+	ArOH	Prep Phenols	None
ArN_2^+	H_3PO_2	H^- on Ar^+	ArH	Replace NO_2 on Ring with H	None
"Quat" Amine $RCH_2CH_2N(CH_3)_3^+ Br^-$	1) Ag_2O or OH- 2) Heat loses $(CH_3)_3N$	E2	Alkene $RCH=CH_2$	Gives <u>least</u> substituted alkene <u>Hoffman Elimination</u>	None

Table XIV

Reagent code list for

reactions of carbohydrates

REACTIONS OF SUGARS CODE LIST					
STARTING MATERIAL	REAGENT CODE	MECHANISM	PRODUCT	USES	COMMENTS
KETO SUGAR D OR L	OH-	enolization	ALDO SUGAR	SUGAR ISOMERIZATION	KETO SUGAR GIVES POSITIVE TOLLENS TEST DUE TO THIS!
ANY ALDO OR KETO SUGAR	$NaBH_4$	Hydride reduction	polyol	SUGAR REDUCTION	
ANY ALDO OR KETO SUGAR	$Ag^{+1}(NH_3)_2$ OH- Tollens reagent	Oxidation	Acid Sugar and Ag metal COOH on Terminal of Sugar	SUGAR OXIDATION	Silver mirror means reducing sugar with hemiacetal or free aldehyde group TEST FOR GLUCOSE!
ALDO SUGAR	$Cu^{+2}(NH_3)_4$ Blue Fehlings Solution	Oxidation	Acid Sugar and Cu_2O COOH on Terminal of Sugar	SUGAR OXIDATION	Red Cu_2O means reducing sugar with hemiacetal or free aldehyde group TEST FOR GLUCOSE!
ALDO SUGAR	Br_2	Oxidation	Acid Sugar COOH on Teminal of Linear Sugar	SUGAR OXIDATION	
ALDO SUGAR	HNO_3	Oxidation	Acid Sugar COOH on Teminal of Linear Sugar	SUGAR OXIDATION	
ALDO SUGAR	1) HCN 2) H_2/ $BaSO_4$ 3) H_3O^+	Cyanohydrin then hydrolysis	ALDO SUGAR WITH ONE MORE CARBON	SUGAR SYNTHESIS	New sugar mixture of enantiomers at newly created site Kiliani-Fischer Synthesis
ALDO SUGAR	1) NH_2OH 2) Ac_2O 3) OH^-	Oxime then dehydration to cyanohydrin	ALDO SUGAR WITH ONE LESS CARBON	SUGAR SYNTHESIS	Wohl Degradation

Alpha (Axial) cyclic sugar	OH- or H_3O+	Ring opening to free aldehyde	Beta (equatorial) cyclic sugar (predominates)	CYCLIC ISOMERIZATION TO MOST STABLE FORM	MUTAROTATION
Alpha or Beta cyclic sugar	ROH/H_3O^+	Ether formation at anomeric carbon	Glycoside RO at anomeric carbon	Protects sugar from mutarotation Not reversible to hemiacetal at anomeric carbon	Negative Tollens Test! No aldehyde present
Sucrose or other cyclic sugar with no hemiacetal carbon	Ag^+, NH_3 OH- Tollens reagent or $Cu^{+2}(NH_3)_4$ Blue Fehlings Solution	NONE!	NR		Nothing to Oxidize

References:

1) John McMurry, "Organic Chemistry, 7th Edition", Brooks-Cole Publishing Co., 2007.

2) Paula Bruice, "Organic Chemistry, 5th Edition", Prentice Hall., 2007.